

PCTWORLD INTELLECTUAL
Inter

INTERNATIONAL APPLICATION PUBLISHED



WO 9604359A1

(51) International Patent Classification⁶ :

C11D 11/04, 17/06

A1

(43) International Publication Date: 15 February 1996 (15.02.96)

(21) International Application Number: PCT/EP95/02935

(22) International Filing Date: 24 July 1995 (24.07.95)

(30) Priority Data:

9415904.3

5 August 1994 (05.08.94)

GB

(71) Applicant (for AU BB CA GB IE KE LK MN MW NZ SD SG SZ TT UG only): UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB).

(71) Applicant (for all designated States except AU BB CA GB IE KE LK MN MW NZ SD SG SZ TT UG): UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).

(72) Inventors: DHALEWADIKAR, Shashank, Vaman; 3A Agrasa, Hindustan Lever Research Centre Flats, Andheri (East), Bombay 400 099 (IN). DHANUKA, Vinodkumar, Ramniranjan; 306 Parijat, Lallubhai Park Road, Vile Parle (West), Bombay 400 056 (IN). MISTRY, Niraj, Dhansukhlal; 13 Hingh Bhuvan, 62 Sahar Road, Andheri (East), Bombay 400 069 (IN). PACHA, Fakhruddin, Esmail; B-11 Nazir Apartments, 139 Azad Road, Vile Parle (East), Bombay 400 057 (IN).

(74) Agent: GEARY, Stephen; Unilever plc, Patent Division, Colworth House, Sharnbrook, Bedford MK44 1LQ (GB).

(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG).

Published*With international search report.**Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.*

(54) Title: GRANULATION IN A FLUIDISED BED

(57) Abstract

A process for the manufacture of detergent powders involving fluidising a particulate material comprising a neutralising agent, preferably in a fluid bed, contacting LAS acid with the fluidised material to effect neutralisation and optionally adding a flow aid to the material either prior, during or subsequent to the addition of LAS acid is disclosed.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

GRANULATION IN A FLUIDISED BED

5 The present invention relates to a detergent composition having a low bulk density (BD) and a process for its production by dry neutralisation and further envisages the use of a fluidised bed for manufacture of such detergent compositions.

10 It is known in the art to obtain detergent powders by the step of spray drying. However, such a process of spray drying is attended with the disadvantage that it is both capital and energy intensive and, consequently the product obtained therefrom is expensive. Simultaneously, a
15 distinct advantage accruing from such a process is that the powders have a low bulk density of 350 to 600 g/L.

Henkel 4304062 describes the production of a cleaning active surfactant granulate in which an anionic surfactant in acid form is neutralized with an aqueous alkali solution
20 under high gas pressure in a granulation and drying chamber. In this process the drying of a non-surfactant liquid component by using hot air is an essential step.

The process of dry neutralization for preparing detergent
25 powders is known in the art but this often results in powders having a high bulk density. Indian patent no. 166307, (Hindustan Lever Ltd) refers to specific use of an internal recirculating fluidised bed and mentions that use of a conventional fluidised bed will lead a lumpy and
30 sticky process.

East German Patent No. 140 987 (VEB Waschmittelwerk) discloses a continuous process for the production of granular washing and cleaning compositions, wherein liquid
35 components such as nonionic surfactants or the acid precursors of anionic surfactants are sprayed onto a

- 2 -

powdered builder material, especially sodium tripolphosphate (STPP) having a high phase II content to obtain a product with bulk density ranging from 530 - 580 g/L. However, the process according to the said East
5 German Patent is restricted to the use of STPP having a high phase II content.

GB1404317 discloses the preparation of a detergent powder of low or moderate bulk density by a dry neutralization
10 process. Sulphonic acid is mixed with an excess of soda ash in the presence of sufficient water to initiate the neutralization reaction but not enough to wet the resulted product which is in the form of a free-flowing powder. The process is carried out in a mixing apparatus, for example a
15 ribbon blender, planetary mixer or air transfer mixer. In a mixing apparatus, the particulate detergent material is subjected to compressive forces which may lead to an increase in bulk density.

20 We have now found that the disadvantages of the prior art maybe obviated by neutralising an acid precursor of a surfactant in a fluidised bed to produce a powder having a low bulk density.

25 According to the first aspect of the invention, there is provided a process for the production of a detergent composition having a low bulk density which comprises contacting an acid precursor of an anionic surfactant with a neutralizing agent in a fluidised bed to effect
30 neutralisation of the precursor whereby the detergent composition is obtained.

The invention provides in a second aspect, a process for the production of a particulate detergent composition
35 having a low bulk density which comprises feeding a particulate material comprising a neutralising agent and

- 3 -

optionally a detergency builder in a fluidisation zone, fluidising the material, contacting a liquid precursor of an anionic surfactant with the fluidised material to effect at least partial, and preferably substantially complete, neutralisation of the acid precursor and to effect the formation of detergent particles comprising the neutralised precursor acid.

Preferably the fluidisation zone is provided by means of a fluid bed.

According to a further aspect of the invention, there is provided a process for the production of a particulate detergent composition having a low bulk density which comprises:-

- i. introducing a particulate material comprising a builder and a neutralizing agent into a fluidised bed;
- ii. introducing linear alkyl benzene sulphonate (LAS) acid into the said bed over a sufficient time to effect at least partial neutralization of the acid and to attain the required properties of the powder.

The invention also provides a detergent composition obtainable by a process as defined in the claims.

The process may be carried out in either batch or continuous mode of operation as desired. The term "detergent composition" as used herein includes a detergent material which may be mixed with other conventional materials for example bleaches and enzymes to produce a fully formulated product and also a detergent component, often referred to as an adjunct, which may be treated further to produce a detergent material which may then be mixed with other materials as desired.

- 4 -

In accordance with this invention the process envisages dry neutralization of the acid precursor of an anionic surfactant with a neutralising agent by fluidisation of the neutralising agent; preferably the process is carried out in a fluidised bed. The process of dry neutralisation refers to at least partial and preferably substantially complete neutralisation of the acid precursor while the mixture remains in particulate form. Suitably, addition of the acid precursor is controlled so that it does not accumulate in the unneutralised form in the detergent composition.

The neutralising agent is suitably particulate and comprises an alkaline inorganic material, preferably an alkaline salt. Suitable materials include alkali metal carbonates and bicarbonates for example sodium salts thereof.

The neutralising agent is suitably present at a level sufficient to neutralise fully the acid precursor. If desired a stoichiometric excess of neutralising agent may be employed to ensure complete neutralisation or to provide an alternative function, for example building, in the case of sodium carbonate.

In addition to the anionic surfactant obtained by the neutralisation step further anionic surfactants or nonionic, cationic, zwitterionic, amphoteric or semipolar surfactants and mixtures thereof may be added at a suitable time. Suitable surfactants include those generally described in "Surface active agents and detergents " Vol I by Schwartz and Perry. Thus if desired soap derived from saturated or unsaturated fatty acids having C_{12} to C_{15} carbon atoms may also be present as an anionic surfactant.

- 5 -

The detergent active is suitably present at a level of 5 to 40%, preferably 12 to 30% by weight of the detergent composition.

5 The detergent composition suitably contains a detergency builder. The builder may be introduced with the neutralising agent and/or added subsequently as desired. Preferably, the builder is introduced with the neutralising agent.

10

Any conventional builder may be employed; suitable builders include sodium carbonate, zeolite, sodium tripolphosphate (STPP) sodium citrate and/or high surface area calcite. The builder can also consist of one of the above singularly or in combination with other builders.

15

The builder and neutralising agent may be the same material, for example sodium carbonate, in which case sufficient material will be employed for both functions.

20

The builder is suitably present at a level of 15 to 65% and preferably 15 to 50% by weight of the detergent composition.

25 Detergent powder obtained by the present invention suitably has a low bulk density in the range 350 to 650 g/l, or 450 to 650g/l, for example, in the proximity of 500 g/L and is thus comparable to a bulk density obtained by the method of spray drying.

30

Optionally and preferably a flow aid is incorporated into the composition. The flow aid may be mixed with the neutralising agent and, if present, builder prior to or subsequent to partial or complete addition of the acid
35 pr cursor. It is especially preferred that the flow aid b added prior to or after partial introduction of the acid

- 6 -

precursor as a significant reduction in the bulk density of the final powder may be achieved.

5 The flow aid is suitably present in an amount of 0.1 to 15% by weight of the detergent composition and more preferably in an amount of 0.5 to 5%.

10 Suitable flow aids include crystalline or amorphous alkali metal silicate, calcite, diatomaceous earth, silica, for example precipitated silica, magnesium sulphate, and calcium carbonate, for example precipitated calcium carbonate. Mixtures of these materials may be employed as desired. In the preferred embodiment, the flow aid is Dicalmol.

15 The composition may also comprise a particulate filler which suitably comprises an inorganic salt, for example sodium sulphate and sodium chloride. The filler may be present at a level of 5 to 50% by weight of the composition.

20 The detergent composition produced according to the invention suitably comprises the detergent active and builder and optionally one or more of a flow aid, a filler and other minor ingredients such as colour, perfum, fluorescers, bleaches, enzymes.

25 We have further found that a significant reduction in bulk density may be secured by selecting raw materials having certain particle size characteristics.

30 Suitably the particulate material(s) have a particle size distribution such that not more than 5% by weight of the particles have a particle size greater than 250 μ . It is also preferred that at least 30% by weight of the particles have a particle size below 75 μ . Suitably the particulate

- 7 -

material(s) has an average particle size below 200 μ to provide detergent powders having a particularly desired low bulk density.

5 If desired a controlled amount of water may be added to facilitate neutralisation. The water may be added in amounts of 0.5 to 2% by weight of the final detergents composition. Any such water is suitably prior to or together or alternating with the addition of the acid precursor.

10 Suitably the particulate material is introduced into a fluidised bed and the required amount of LAS acid is then introduced preferably by spraying onto the said material and preferably from the top. If present the flow aid maybe introduced with the starting material. However, it is preferred that the flow aid be added after part introduction of part of the LAS acid to obtain a lower bulk density.

20 The fluid bed is suitably operated at a temperature of ambient to 60°C. The air flow is sufficient to cause fluidisation and is preferably in the range 0.6 to 1 ms⁻¹. Fluidisation of the solid material is an essential feature of the present invention as this facilitates neutralisation and granulation whilst keeping the particles apart. This is to be contrasted with mixing processes in which the particles, are intentionally contacted and compressed, which may lead to higher bulk density powder and poorer powder properties.

30 The invention is illustrated by the following non-limiting examples.

EXAMPLES 1 to 19

35 A powdered builder/inorganic alkaline material (in Examples 1 to 4, sodium carbonate performed both functions) and a

- 8 -

filler was introduced into a fluid bed and was fluidised by operating at a superficial air velocity above the minimum fluidisation velocity. The temperature in the fluid bed was from ambient to 60°C. Linear alkyl benzene sulphonic acid (LAS acid) was sprayed onto the powdered mix in the fluid bed.

The relative amounts of the various components of the composition were varied and are listed below in Table 1.

10

Examples 1 to 3 illustrate the effect of incorporation a flow aid (in this case Dicamol) to the composition at different points in the process. In Example 1 the flow aid was not added to the material. In Example 2, the flow aid was added to the starting material prior to the introduction of LAS acid. In Example 3, the flow aid was added after introduction of 50% of the LAS acid. Example 4 illustrates the benefits obtained in employing a fine grade of particulate material. The results are shown below in Table 1.

20

TABLE 1

	EXAMPLE 1	EXAMPLE 2	EXAMPLE 3	EXAMPLE 4
LAS	17	17	17	1
Soda Ash	30	30	30	30
Dicamol	-	2*	2**	2**
Salt	45	43	43	-
Fine salt	-	-	-	43
BD (g./L)	687	625	603	546
DFR (ml/sec)	85.72	96.77	88.23	93.8
*ROD (%)	81.6	80.6	82.3	82.5

25

30

*Rate of Dissolution

*Dicamol added initially

35

**Dicamol added after 50% LAS

- 9 -

The rate of dissolution of the powder was determined by adding powder to 1l of water to provide a concentration of 1.4%, mixing at 100 rpm and measuring the conductivity of the solution until a constant reading was reached. The figures quoted refer to the level of powder dissolved after about 90 seconds.

Examples 2 and 3 illustrate that a significant reduction in bulk density may be achieved by addition of the flow aid either prior to or subsequent to introduction of part of the LAS acid.

Further powders, Examples 5 to 19, as detailed below in Tables 3 to 5 were prepared according to the process described for Examples 1 to 4 and various raw materials having a different particle size distribution were employed. Table 2 summarises the size distribution of the various materials.

TABLE 2

Properties of various raw materials					
Size distribution	Soda ash	Na ₂ SO ₄	Salt	Fine Salt	STPP
(micron)	%wt				
>500	1.8	0.12	1.78	1.00	0.94
500 - 250	2.06	0.60	80.40	1.26	1.40
250 - 150	6.52	21.90	14.80	10.02	6.86
150 - 100	26.20	55.14	2.88	21.80	24.88
100 - 75	16.20	8.56	0.14	24.07	7.92
<75	47.14	13.68	-	36.83	58.00
Mean particle size (u)	92.7	138.2	360.30	112.5	85.7
BD, g/L	508	1,347	1,070	997	649
DFR, ml/sec	No flow	83.33	142.85	No flow	No flow

- 10 -

Table 3

	Examples	5	6	7	8	9	10
	LAS %	17.0	20.0	23.0	23.7	25.0	27.1
	Moisture, %	6.8	6.0	4.8	6.0	4.5	5.1
5	STPP, %	35.0	22.0	35.0	35.0	25.0	25.0
	Soda ash, %	22.0	20.0	22.0	22.0	20.0	20.0
	Fine salt, %	-	30.0	-	-	16.0	15.0
	Alk.silicate, %	-	-	-	-	-	1.0
	Bulk density, g/L	500	510	500	490	500	495
10	DFR, ml/sec	100	120	120	120	100	88

TABLE 4

15	Examples	11	12	13	14	15
	LAS Acid, %	28.5	28.7	29.13	29.6	31.1
	Moisture, %	4.5	6.7	6.2	7.4	6.8
	STPP, %	25.0	35.0	25.0	35.0	35.0
	Soda ash, %	20.0	22.0	20.0	22.0	22.0
20	Fine salt, %	16.0	-	-	-	-
	Na ₂ SO ₄ , %	-	-	16.0	-	-
	Bulk density, g/L	514	470	510	500	520
	DFR, ml/sec	120	100	88	102	115

25

Table 5

Example	16	17	18	19
LAS, %	17.0	17.0	17.0	13.0
Soap, %	-	-	-	4.0
Soda ash, %	22.0	30.0	35.0	20.0
STPP, %	35.0	-	-	35.0
HSA calcite, %	-	-	16.0	-
Moisture, %	6.8	3.5	3.0	4.0
BD, g/L	500	530	480	500
DFR, ml/sec	100	100	120	150

Tables 3 and 4 show the results for STPP built powders containing active in the range of 17 to 31%. The soda ash and STPP had a similar particle size distribution as shown in Table 2 and formulations based on such builder systems resulted in products with bulk density close to 500 g/L. Table 5 shows powders based on various builder systems, i.e. STPP, soda ash and HSA calcite. Both the soda ash and STPP built formulations resulted in powders with BD of about 500 g/l whereas formulations based on HSA calcites resulted in powders with bulk density lower than 500 g/L. Example 19 relates to a mixed active system containing 13% LAS AD and 4% soap and resulted in powder with bulk density of 500 g/L.

- 12 -

CLAIMS

- 1 A process for the production of a detergent composition having a low bulk density which comprises contacting an acid precursor of an anionic surfactant with
5 a neutralizing agent in a fluidised bed to effect neutralisation of the precursor whereby the detergent composition is obtained.
2. A process for the production of a particulate
10 detergent composition having a low bulk density which comprises feeding a particulate material comprising a neutralising agent and optionally a detergency builder in a fluidisation zone, fluidising the material, contacting a
15 liquid precursor of an anionic surfactant with the fluidised material to effect at least partial, and preferably substantially complete, neutralisation of the acid precursor and to effect the formation of detergent particles comprising the neutralised precursor acid.
- 20 3 A process for the production of a particulate detergent composition having a low bulk density which comprises:-
i. introducing a particulate material comprising a builder and a neutralizing agent into a fluidised bed;
25 ii. introducing linear alkyl benzene sulphonate (LAS) acid into the said bed over a sufficient time to effect at least partial neutralization of the acid and to attain the required properties of the powder.
- 30 4. A process according to any preceding claim in which the neutralising agent comprises an alkaline inorganic material, preferably an alkali metal carbonate.
- 5 A process according to any preceding claim
35 comprising the step of adding one or more of flow aids in an amount of 0.1-15% by wt. of the composition.

- 13 -

6. A process according to any preceding claim wherein the flow aid is added after partial addition of the acid precursor.
- 5 7. A process according to any one of claims 1 to 5 wherein the flow aid is added before addition of the acid precursor.
- 10 8. A process according to any preceding claim wherein the flow aid is one or more of dicamol, crystalline or amorphous alkali silicate, calcite, diatomaceous earth, precipitated silica, magnesium sulphate.
- 15 9. A process according to any of the preceding claims wherein the neutralising agent and other material particulate have a particle size distribution such that not more than 5% of the particles have a particle size greater than 250 μm and more than 30% of the particles have a particle size of less than 75 μm .
- 20 10. A detergent composition or component therefor obtainable by a process according to any preceding claim.

INTERNATIONAL SEARCH REPORT

Inter: nal Application No
PCT/EP 95/02935

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D11/04 C11D17/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 353 976 (PATERSON ZOCHONIS UK LTD) 7 February 1990 see page 3, line 14 - line 16; claims 1-15; examples ---	1-4, 10
X	DD,B,140 987 (VEB WASCHMITTELWERK) 9 April 1980 cited in the application see page 4, line 11 - line 17; claims 1-4; examples ---	1-4, 10
A	DE,A,42 32 874 (HENKEL KGAA) 31 March 1994 see claims 1-8; examples ---	1, 4, 10
A	GB,A,1 404 317 (BELL CHEMICALS PTY) 28 August 1975 cited in the application see claim 1 ---	1, 4, 10
-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

20 December 1995

Date of mailing of the international search report

8.01.96

Name and mailing address of the ISA

European Patent Office, P.B. 3818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+ 31-70) 340-3016

Authorized officer

Grittern, A

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/EP 95/02935

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,3 425 948 (OTRHALEK JOSEPH V ET AL) 4 February 1969 see column 3, line 48 - column 4, line 65; claims ---	1,3-5,8, 10
A	GB,A,1 369 269 (COLGATE PALMOLIVE CO) 2 October 1974 see claims; examples ---	1,4,10
A	US,A,4 734 224 (BARRETT JOHN H ET AL) 29 March 1988 see claims ---	1,4
A	DATABASE WPI Section Ch, Week 8703 Derwent Publications Ltd., London, GB; Class D25, AN 87-019854 & RO,A,88 903 (DERO INTR DETERGEN) , 30 June 1986 see abstract -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 95/02935

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0353976	07-02-90	AU-B- 622925	30-04-92
		AU-B- 4049289	05-03-90
		DE-D- 68911053	13-01-94
		DE-T- 68911053	31-03-94
		EP-A- 0404865	02-01-91
		ES-T- 2047677	01-03-94
		WO-A- 9001536	22-02-90
		HK-A- 48495	07-04-95

DD-B-140987		NONE	

DE-A-4232874	31-03-94	CN-A- 1087945	15-06-94
		WO-A- 9407990	14-04-94
		EP-A- 0663005	19-07-95

GB-A-1404317	28-08-75	NONE	

US-A-3425948	04-02-69	AU-A- 1591866	

GB-A-1369269	02-10-74	AU-B- 3800572	19-07-73
		BE-A- 778811	30-05-72
		CH-A- 569079	14-11-75
		DE-A- 2203552	10-08-72
		FR-A, B 2124284	22-09-72

US-A-4734224	29-03-88	NONE	
